Light Metals 2011 *Edited by: Stephen J. Lindsay*
TMS (The Minerals, Metals & Materials Society), 2011

TOWARDS ELIMINATING ANODE EFFECTS

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Keywords: Anode Effect, Anode Current Density, Incipient AE Logic

Abstract

It has been established that the atmosphere contains appreciable amount of per fluorocarbon (PFC) gases. These are powerful greenhouse gases with extremely long lifetime.

Although these gases are being used in the semiconductor industry, it has been established that aluminium smelters are their main source. Emissions of PFC Gases from the aluminium industry have therefore become an environmental issue.

The PFCs are emitted from an aluminium reduction cell when it is on an 'anode effect'. The exact nature of the onset of an anode effect is still shrouded in mystery. However, an astounding reduction in number of anode effects has been achieved by understanding, attributing and implementing a strict process control regime to eliminate assignable causes.

Dubal's progress in reducing anode effect frequency to less than 0.05 AE/pot-day in a sustained manner in poline 5B has been discussed and presented.

Introduction

The IAI survey [1] shows an overall 86% reduction in the emission rate for PFCs per tonne of aluminium produced between 1990 and 2007, equating to a 74% reduction in total emissions as CO_2 equivalent. The reduction in emission rate is despite the doubling of metal production over the same period.

Industrialization and rapid economic growth are major contributing factors to the increase in greenhouse gas emissions, global warming and climate change. The declining rate of PFC emissions is the result of the industry's efforts to reduce the frequency, and the duration of the anode effects in pot line cells. This has been further enhanced through the use of alumina point feeding systems and computer feed control programmes that reduce anode effect frequency. The ongoing phasing-out of older technologies and their replacement with more modern technology, wherever economically justified, is also assisting in decreasing relevant emissions.

Dubai Aluminium Company (Dubal) continues its untiring efforts in reducing PFC emissions. It commissioned Potline 5B in the year 2007, figure 1. The potline houses D20 cell design. The potline amperage was gradually raised from 240 to 260 kA. The cells operate on an anode current density of 1.045 A/cm2 which is understandably on the higher end in the industry. It was therefore a very challenging and daunting task to lower the AE frequency in this potline. Initially, the anode effect frequency in the potline was 0.31 AE/cell/day and this has been brought down to ~0.05 AE/cell/day by a series of measures.

Figure 1. Potline 5B

The Anode Effect

During normal electrolysis the produced anode gas is a mixture of carbon oxides, with CO_2 being the dominant product formed according to the overall reaction,

$$2Al_2O_3 + 3C = 4Al + 3CO_2$$

Normally this reaction proceeds at an anode potential of Al^{3+}/Al of ~1.6 volt, with the increase in potential above the minimum (~1.18V) being due to both concentration and reaction polarisation [2, 3]. The exact magnitude of the anode potential is a complex function of the anode carbon quality, the electrolyte temperature, the dissolved alumina concentration, and operating current density.

Modern smelting operation is moving towards favouring lower dissolved alumina concentration (for better control and resulting efficiency) and higher anode current densities (for increased productivity) and this increases the concentration polarisation, and hence anode potential.

The next possible electrochemical reaction product has been shown to be COF_2 [4, 5] according to the overall reaction,

$$Al2O_3 + 3C + 2AlF_3 = 4Al + 3COF_2(g).$$

Thermodynamic data suggest this should occur at an anode potential of Al^{3+}/Al ~1.7 to 1.8 V, depending on the alumina and aluminium fluoride concentrations [6].

Coincidentally the magnitude of increase is consistent with the working range of control limits " resistance" increase during under and over feed strategy.

The exact mechanism of the above reaction, and the overall kinetics is less certain, but the presence of $3COF_2(g)$ [4]. and its electrochemical formation [5] has been established in carefully controlled laboratory research. It is clear that passivation of the electrode surface plays a role, but the cause and form that it takes is a subject of debate.

Figure 2 shows the controlled voltage sweeps of a small cell at different alumina concentrations [7]. The electrode process changes through concentration polarisation and subsequently after a limited amount of electrolysis passivation causes the current to drop to almost zero.

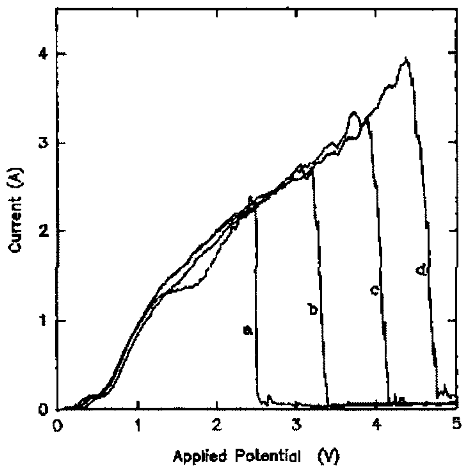

Figure 2: Potentiodynamic voltammogram of a carbon anode electrolysed in cryolitic electrolyte.
(a) =0.75 wt% Al_2O_3, (b) =1.75 wt% Al_2O_3, (c) =2.75 wt% Al_2O_3, (d) =4.55wt% Al_2O_3. From Haverkamp[6]

Under the approximately constant current conditions of an operating smelter, the highly resistive nature of the passivating film causes an ohmic increase in cell voltage (often manifested by arcing) as the electrolysis continues, figure 3.

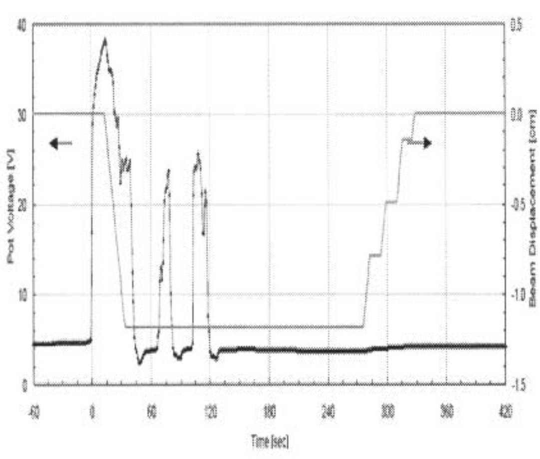

Figure 3. The rapid rise in voltage following the onset of an anode effect

Measurement in operating cells has also demonstrated that an anode effect often starts in a region of a cell causing a decrease in the current of the affected anode and a corresponding rise in the current of the others [8]. This implies that cells have concentration gradients, or varying current densities at different zone.

Issues Impacting AE Frequency

Following factors can all contribute to the onset of an anode effect,

- Addition of alumina too late or too slowly, i.e. below the limit sustainable by the operating anode current density.
- On occasions, the anode current density exceeding the critical current density.
- Maintenance issues within the cell, e.g. blocked feeder holes, empty ore bins, hindered transfer of alumina into the feeder hole.
- Delayed sensing of the voltage rise.
- Insufficient depth of immersion of anodes (very low bath level), anode burn off, etc.

The potline work pattern is a 4-shift work cycle – metal tapping▶idle▶anode setting▶idle shift. An analysis of the anode effects in D20 cells was performed as under:

- The majority of anode effects occurred during anode setting operation[9], figure4. The anode setting activity temporarily increases anode current density probably to the critical density threshold which triggers an anode effect.

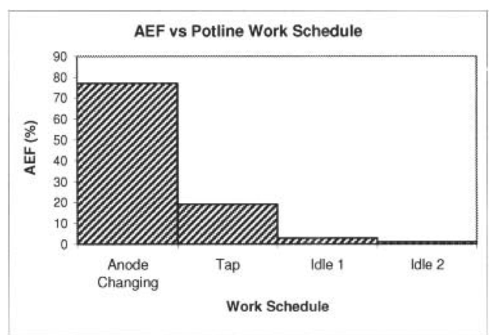

Figure 4. AEF vs Work Schedule

- The alumina feed cycle is super fast (SF)▶over feed (OF)▶base feed (BF)▶under feed (UF). The super fast feed is for a very short duration. The anode effects were concentrated in the over feed window, figure 5.

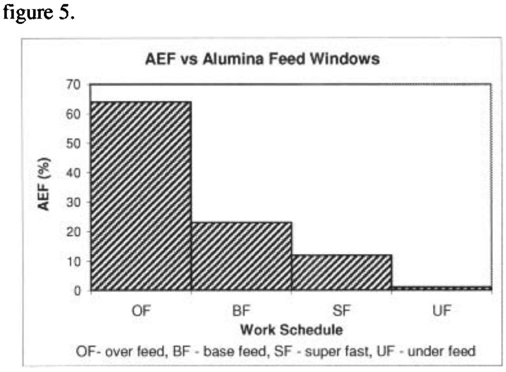

Figure 5. AEF vs Alumina Feed Windows

This means that the demand feed was not always able to efficiently react in time to prevent an anode effect. Hence digital signal filtering becomes a contributing issue.

- It was established in the other potlines that potline amperage increase had an adverse effect on AE frequency [9], figure 6. The amperage increase has pushed the anode current density and also the rate of alumina depletion.

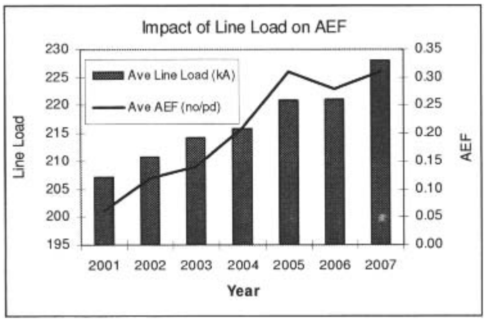

Figure 6. Impact of Line Load increase on AEF.

- The Dense Phase System for transporting alumina to the cell hoppers primarily operates on high pressure, low velocity concept. A drop in pressure was found to have a profound impact on hopper filling and consequently on the anode effect frequency.

- Pencilling of crust breaker tips lead to insufficient alumina quantity reaching the bath.

- Bath build up on the crust breaker hindered the delivery of the prescribed alumina dose at the right time as illustrated in figure 7.

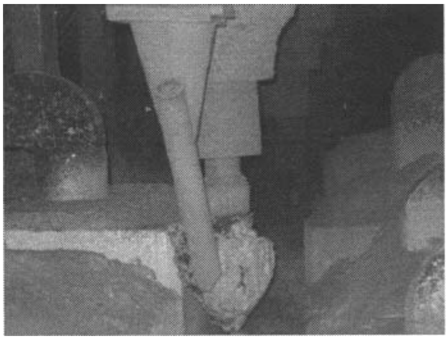

Figure 7. Bath Build Up on Crust Breaker Tip.

- Unexpected variability in alumina delivery from the conveying and delivery system that is installed in some of the Dubal potlines. A typical problem was an unannounced massive surge in the delivery of alumina fines to a cell or a small group of cells. Analysis of anode effects in relation to 'fines' on a sample basis confirms this, figure 8.

  A weak correlation was observed between AE frequency and other parameters such as bath chemistry and bath temperature. An unstable cell can trigger anode effects at higher alumina concentrations [10]. This is attributed to difference in alumina concentration gradients between the bulk of the bath and to the difference in gas coverage of the anode surface.

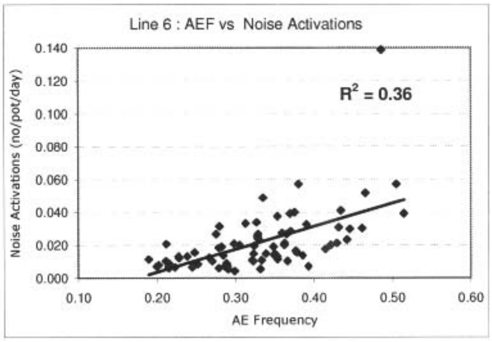

Figure 8. Impact of Noise Activations on AEF

Actions & Results

First, the operating practices were revisited and fine tuned. Later, logic to 'kill' an incipient anode effect was developed and introduced.

- The anode setting and anode covering practice were designed to minimise spillage, figure 9. The controls were specifically targeted to permit a maximum amount alumina feeding from point feeds.

  The changes included auto anode mark transfer – this minimized subsequent anode adjustments to achieve an optimum current distribution and also minimized the need to redress the anodes. The anode top cover thickness and the composition of the cover material were monitored closely – this helped in minimizing variations in the 'anode top heat losses'.

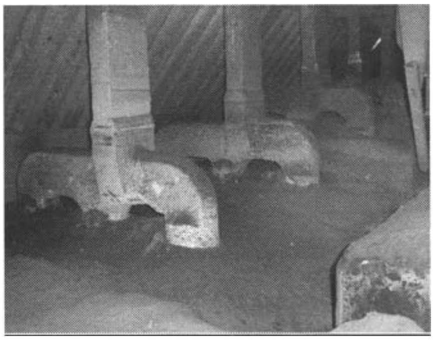

Figure 9. Uniform Anode Top Ore Cover

- The bath chemistry controls were optimised and designed for cells to operate within a narrow superheat. The bath chemistry control strategy was followed up closely and would take into account the natural cell variations, figure 10.

- The operation at the end of an underfeed would provide a minimum of overfeed alumina dumps so that the risk of muck formation was minimised.

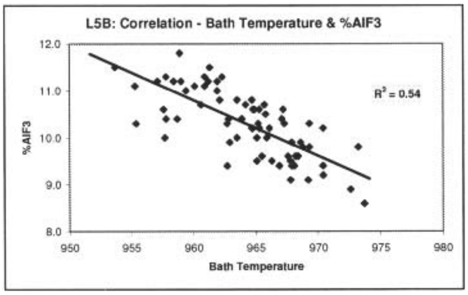

Figure 10. Correlation of xs AlF3 & Bath Temp.

- Process variations through normal operations and control were minimised; where the cell got out of the expected control band, diagnostics were performed prior to taking extreme steps. The principle was to operate the cells on very similar anode-to-cathode distance table 1. The poor performing cells were diagnosed in terms of the voltage drop (or resistance) in different segments, current distribution, and metal pad reserve; corrective actions applied as appropriate.

Cell	Lining+External Drop (mV)	Bath Res (uOhm)	Actual BRS	Diff Actual - S	BRSP chang	New BRSP	Diff New - S
181	485	7.00	11.80	0.25	0.25	11.65	0.00
182	605	7.29	12.40	-0.16	0.15	12.15	0.01
183	540	7.36	11.80	-0.07	0.05	11.85	-0.02
184	500	7.78	12.30	0.34	-0.35	11.95	-0.01
185	580	7.39	12.00	-0.06	0.05	12.05	0.01
186	605	7.79	12.50	0.38	-0.35	12.15	0.01
187	590	7.55	12.30	0.12	-0.10	12.10	0.02
188	530	7.35	11.75	-0.08	0.10	11.85	0.02
189	540	7.40	11.90	0.03	-0.05	11.85	-0.02
190	575	7.57	12.10	0.08	-0.10	12.00	-0.02
191	545	7.58	12.00	0.10	-0.10	11.90	0.00
192	550	7.47	11.95	0.01	-0.05	11.90	-0.02
193	580	7.38	11.90	-0.06	0.05	11.95	-0.01
194	570	7.44	12.00	0.00		12.00	0.00
195	570	7.49	12.05	0.05	-0.05	12.00	0.00
196	575	7.76	12.35	0.27	-0.35	12.00	-0.02
197	535	7.53	11.95	0.10	-0.10	11.85	0.00
198	540	7.36	11.80	-0.03	0.05	11.85	-0.02
199	575	7.41	12.00	-0.02		12.00	-0.02
200	545	7.54	12.00	0.10	-0.10	11.90	0.00
201	605	7.38	12.30	-0.04	0.05	12.35	0.01
202	560	7.48	12.00	0.04	-0.05	11.95	-0.01
203	570	7.34	11.90	-0.10	0.10	12.00	0.00
204	650	7.45	12.15	0.02		12.35	0.02
205	590	7.25	11.90	-0.14	0.20	12.10	0.02
206	590	7.40	12.05	-0.03	0.05	12.10	0.02
207	705	7.28	12.40	-0.16	0.15	12.55	-0.01
208	630	7.29	12.10	-0.15	0.15	12.25	0.00
209	560	7.40	12.00	0.04	-0.05	11.95	-0.01
210	580	7.34	11.95	-0.09	0.10	12.05	0.01

Table 1. Example of cell voltage balance

- The next stage was to observe the anode effects and feeding characteristics. The resistance curves were carefully analysed and inferred. A programme was developed to recognise and 'kill' an incipient anode effect. It involved lowering the anodes to short them with metal, breaking the crust and feeding alumina at a rapid rate. The success rate in the 'incipient AE quench logic is normally greater than 90%.

The results were encouraging and brought down the anode effect frequency by nearly 78%, table 2.

Parameter	Unit	Before			After
		Year 2007	Year 2008	Year 2009	Year 2010
AE Freq.	No/ cell/ day	0.31	0.22	0.19	0.069
AE Durn	Sec.	83	33	47	48

Table 2: AE data – before and after implementing 'incipient AE logic'

Line load in potline 5B was increased gradually from 240 to 260 kA, figure 11. Further amperage increase was limited by the rectifier limitations. The anode size remained unchanged throughout. As a consequence, the anode current density increased to 1.045 A.cm^{-2}. Therefore the objective of being able to operate on a low anode effect frequency was even more challenging.

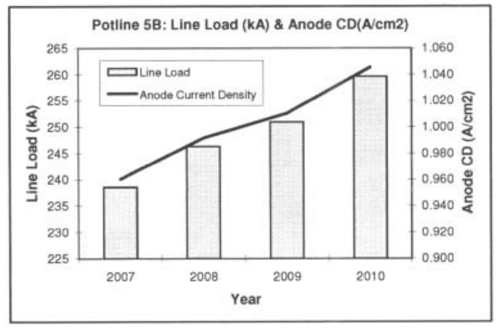

Figure 11. Line Load vs Anode Current Density

After implementing the 'Incipient AE logic', the potline operated on 'zero' anode effects on many days. When examining the potline operating data, the days having AEs were generally preceded by significant interruptions to the alumina feeding, usually associated with compressed air pressure. The issues have since been addressed.

Cell stability has been excellent throughout as shown in a cell trace in figure 13. The 'noise' in the voltage has been very low which is an indirect confirmation that the changes introduced in the feed strategy due to the 'incipient AE logic to have not caused any muck build up.

Despite the current density remaining at 1.045 A.cm^{-2}, current efficiency was maintained at 95.4 - 95.5% level throughout, figure 12. This has been possible due to excellent cell stability and is also a confirmation of the robustness of the cell design.

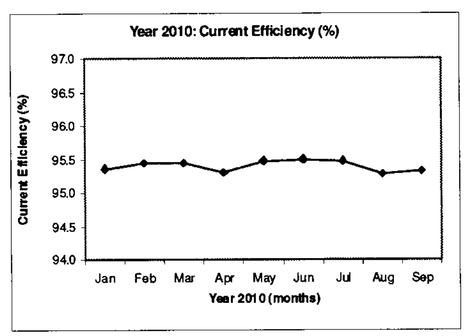

Figure 12. Line 5B – Current Efficiency

Control parameters, such as cathode voltage drop, aluminium fluoride and alumina percentage were monitored and adjustments made to maintain an optimum cell voltage and bath superheat, tables 1 &3

Parameter	Unit	Before			After
		Year 2007	Year 2008	Year 2009	Year 2010
Line Load	kA	238.6	246.3	250.9	260.0
Volts/Cell	V	4.66	4.50	4.53	4.55
Al_2O_3 bath	%	4.5	4.2	4.2	4.0
Ex. AlF_3	%	10.1	10.2	10.2	10.0
Superheat	°C	12.2	10.5	10.2	9.1
ACD	mm	41.2	35.9	34.5	33.3

Table 3: Control Parameters – before & after implementing 'incipient AE logic'

Concluding Comments

Reducing anode effects is a challenge facing aluminium smelters to minimise wastage of energy and reduce green house gas generation.

The amperage in potline 5B has been raised gradually from 240.0 kA to 260.0 kA. Consequently, anode current density increased from 0.965 to 1.045 A.cm^{-2}. This has made the task of reducing anode effects even more daunting.

Compressed air pressure plays an important role in controlling anode effects. The mechanical aspects (crust breakers, feeders, etc) of a cell shall and will continue to interfere with smooth functioning of demand feed. The above challenges make it practically impossible to achieve zero anode effect frequency with our installed hardware.

However, a 78% decrease in anode effect frequency could be achieved by tracking the voltage rise and killing an incipient anode effect. The anode effect frequency could be lowered from 0.31 to ~0.069 AE/cell/day.

The impact of amperage and anode current density increase was kept within the heat balance limits by monitoring the superheat and energy management while ensuring minimum sludge formation as indicated by changes in the cathode voltage drop, cell instability values and alumina content in the bath.

Productivity gains have been achieved by maintaining the current efficiency as a consequence of better controls. All this was achieved whilst maintaining an enviable metal purity of better than 99.90% Aluminium. Further work is in progress towards an ambitious target of <0.01 AE frequency.

Acknowledgement

The authors gratefully acknowledge the guidance, support and encouragement of Dubal management in carrying out this project. .

References

1. International Aluminium Institute, Results of the 2007 Anode Effect Survey, pp 1-6.

2. Richards, N.E. and Welch, B.J. "Anode Overvoltage in Electrolysis of Cryolite-Alumina Melts", Extractive Metallurgy of Aluminium, Vol. 2, Aluminium (Ed. G. Gerard) pp 15-30 (Interscience, New York) (1963).

3. Welch, B.J. "Tech. of Electrolyte Reduction of Alumina by Hall-Heroult Process: I. A Voltage Analysis Under Conditions of Varying Alumina Concentrations". Proc. Aust. I.M. & M., No. 214, pp 1-19 (1965).

4. Dorreen M M S. PhD thesis "Cell Performance and Anodic Processes in Aluminium Smelting Studied by Gas Product Analysis". Univ. of Auckland, (2000)

5. A. J. Calandra, C. E. Castellano and C. M. Ferro, "The Electrochemical Behaviour of Different Graphite / Cryolite Alumina Melt Interfaces Under Potentiodynamic Perturbations" Electrochimica Acta, Vol 24, 1979, pp 425-437.

6. Dorreen, M.M.R., Chin, D., Lee, J., Hyland, M.M. and Welch, B.J. "Sulfur and fluorine containing anode gases produced during normal electrolysis and approaching an anode effect", *Light Metals 1998* pp 311 - 316.

7. Haverkamp R G. PhD thesis "Surface Studies and Dissolution Studies of Fluorinated Alumina" University of Auckland, (1992).

8. J T.Keniry, GC.Barber, M. P.Taylor and B J.Welch, Digital Processing Of Anode Current Signals: An Opportunity For Improved Cell Diagnosis And Control *Light Metals 2001* pp 1225.

9. A. Kumar, A. Zarouni and M. Al Jallaf, Initiatives to Reduce SEF at Dubal, Light Metals, pages 259 – 262.

10. J. Thonstad, et al, 'Aluminium Electrolysis', pp 201 - 206.